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Lamellar-in-lamellar structure of binary linear multiblock copolymers

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A theoretical description of the lamellar-in-lamellar self-assembly of binary A-*b*-(B-*b*-A)$_m$-*b*-B-*b*-A multiblock copolymers in the strong segregation limit is presented. The essential difference between this binary multiblock system and the previously considered C-*b*-(B-*b*-A)$_m$-*b*-B-*b*-C ternary multiblock copolymer system is discussed. Considering the situation with long end blocks, the free energy of the lamellar-in-lamellar self-assembled state is analyzed as a function of the number k of "thin" internal lamellar domains for different numbers m of repeating (B-*b*-A) units and different values of the Flory–Huggins χ_{AB} interaction parameter. The theoretical predictions are in excellent agreement with the available experimental data. © *2008 American Institute of Physics*.
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I. INTRODUCTION

Hierarchically ordered block copolymer and block copolymer–based systems have been extensively investigated during the last decade. They became an attractive subject for experimental[1–15] and theoretical[16–20] investigations due to the possibilities to form structures combining different periodicities. One of the first observations of a double-periodic self-assembled structure involved the self-assembly in polystyrene-*block*-poly(4-vinylpyridine) (PS-*b*-P4VP) diblock copolymers with hydrogen-bonded pentadecylphenol (PDP) side chains to the P4VP block.[1,2] The reported structure has two different periods related to the two different intrinsic length scales: the long length scale period related to the diblock copolymer character of the complexes and the short length scale period involving the separation between the alkyl tails of the PDP side chains and the hydrogen-bonded P4VP blocks.

In the above example we are dealing with one linear block and one comb-shaped block and the short length scale is associated with the "repeat" motive of this comb-shaped block. A branched-type molecular architecture is, of course, not essential, the important point is that the molecular architecture involves two or more intrinsic length scales. Linear multiblock copolymers with two different length scales, e.g., by having one or two end blocks that are significantly longer than the other blocks, serve as one of the simplest examples of a multiblock architecture where the structure-in-structure has been observed as well. As reported in Ref. 4, the formation of a five-layered lamellar-in-lamellar structure was experimentally observed for P2VP-ISISISISI-P2VP undecablock copolymers with two long poly-2-vinylpyridine (P2VP) end blocks and nine short internal alternating polyisoprene (I) and polystyrene (S) blocks, where all chemically different species are mutually incompatible. A "thin" five-layered I-S-I-S-I lamellar structure was formed by the nine short isoprene and styrene blocks within "thick" P2VP layers.[4]

This multiblock copolymer system consisted of three chemically different moieties. That this is also not essential follows from the lamellar-in-lamellar self-assembled state experimentally observed for a undecablock S-ISISISISI-S copolymer with "long" polystyrene end blocks and a middle multiblock consisting of alternating "short" polystyrene and polyisoprene blocks. Compared to the ternary system, however, the number of thin internal layers was reduced from 5 to 3 resulting in a I-S-I thin lamellar structure in between thick polystyrene lamellae.[5]

Using self-consistent field calculations, the existence of double-periodic structures has been also predicted theoretically for linear A-*b*-(B-*b*-A)$_m$ multiblock copolymers with one long A end block as well as for A-*b*-(A-*graft*-B)$_m$ copolymers, where m denotes the number of repeat units. It was concluded that depending on the system parameters such as m and the volume fraction of the end A-block, a two length scale microphase separation will occur: the A end block phase separates from the rest of the polymer and subsequently a short length scale phase separation takes place between the A and B components within the (B-*b*-A)$_m$ (B-*graft*-A)$_m$ domains.[16,17] The phase behavior of A-*b*-(B-*b*-A)$_m$-*b*-B block copolymers has also been studied extensively within the weak segregation limit.[18]

In the present paper we restrict ourselves to the theoretical analysis of the simplest class of multiblock copolymers A-*b*-(B-*b*-A)$_m$-*b*-B-*b*-A with a linear architecture, where the end blocks A are considerably longer than the internal A and B blocks. The scope of the theoretical investigations provided in the present work is to relate the number m of repeating (B-*b*-A) units to the number of thin lamellar layers in the self-assembled lamellar-in-lamellar state.

In the ternary C-*b*-(B-*b*-A)$_m$-*b*-B-*b*-C multiblock copolymer system, due to the assumed strong incompatibility between all three species involved, the middle blocks are

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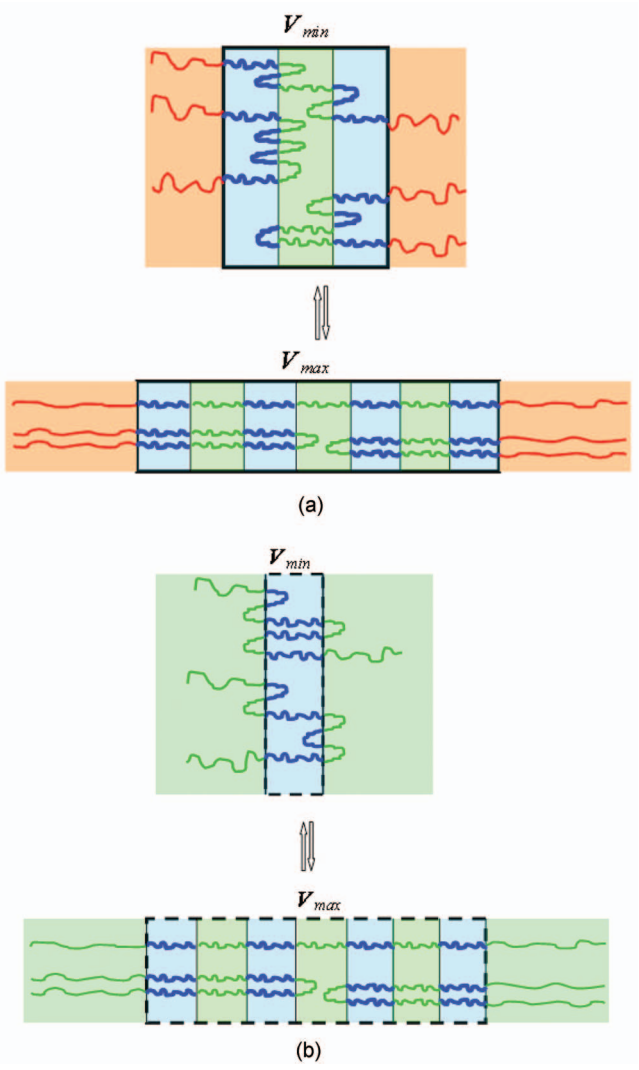

FIG. 1. (Color) Schematic of the minimal and maximal numbers of internal layers for (a) ternary C-*b*-(B-*b*-A)$_m$-*b*-B-*b*-C and (b) binary A-*b*-(B-*b*-A)$_m$-*b*-B-*b*-A system. (a) $V_{\min}=V_{\max}$; (b) $V_{\min}\cong V_{\max}/2$.

never located in the outer C containing regions and, hence, the volume of the internal part formed by the $2m+1$ blocks is the same independent of the number k of internal thin layers formed. On the other hand, in the binary system for $k=1$, only the short B-blocks form the middle thin layer, whereas all the short A-blocks are in the outer thick A-domains. As k increases the number of short A-blocks forming loops inside the layers formed by the long A-blocks gradually decreases. Once all short A-blocks are part of the internal thin lamellar layers, the volume of the internal part has doubled. This essential difference between the ternary and the binary multiblock copolymer systems is schematically illustrated in Figs. 1(a) and 1(b).

An important feature of the system considered here is the presence of two types of A blocks, short and long ones, that are not equivalent. It implies that the binary multiblock copolymer melt is characterized by two different concentration profiles for the segments belonging to the short, respectively, long A blocks. It results in an additional loss of conformational entropy connected to this concentration gradient.

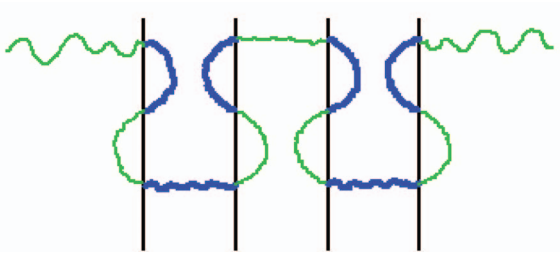

FIG. 2. (Color) Schematic representation of a global bridge A-*b*-(B-*b*-A)$_m$-*b*-B-*b*-A ($m=5$) multiblock copolymer conformation.

To arrive at predictions that agree with the experimental results, a proper consideration of this effect turned out to be essential.

II. THEORY

In this section we will develop a theoretical description of the A-*b*-(B-*b*-A)$_m$*b*-B-*b*-A multiblock copolymer lamellar-in-lamellar self-assembled state. Our objective is to find the dependence between the number m of repeating (B-*b*-A) units and the number k of the internal k-layered structure. We will derive a free energy expression of this A-*b*-(B-*b*-A)$_m$-*b*-B-*b*-A multiblock copolymer self-assembled state depending on the number k of internal domains. The minimum of the free energy as a function of k will determine the equilibrium k-layered structure.

We assume that the statistical segment length a and the monomer volume v are the same for both components. It is also assumed that the degree of polymerization N of the A end blocks is much larger than the degree of polymerization n of the short A- and B-blocks of the internal multiblock, $N\gg n$. The Flory–Huggins parameter χ_{AB} is sufficiently positive, i.e., $n\chi_{AB}\gg 1$, implying the formation of pure A- and B-domains. This allows us to apply the strong segregation theory.

In general, a multiblock chain as part of the lamellar-in-lamellar self-assembled state can assume two different global conformations: either it forms a bridge where the end blocks are located in different layers or it forms a loop where the two end blocks are located in the same layer. Figure 1(b) illustrates these two possibilities.

The average free energy per multiblock copolymer is given by

$$F = xF_{\text{bridge}} + (1-x)F_{\text{loop}} + x\ln x + (1-x)\ln(1-x), \quad (1)$$

where x is the fraction of the global bridges and F_{bridge} and F_{loop} are the global bridge and the global loop free energies. In order to simplify the analysis, we employ the Alexander–De Gennes approximation and assume that the turning point of a global loop is in the middle of the multidomain area formed by the thin lamellar layers (Fig. 1). It implies that the energies F_{bridge} and F_{loop} are approximately equal, $F_{\text{bridge}}\cong F_{\text{loop}}$. Therefore $x\cong 1/2$ and

$$F = F_{\text{bridge}} - \ln 2. \quad (2)$$

The free energy will be given in k_BT energetic units.

A sketch of a possible multiblock bridge conformation is given in Fig. 2 for $m=5$. From here on we will only consider

global bridge conformations.

The total free energy per multiblock copolymer chain consists of the AB interfacial free energy F_{AB}, the conformational free energy F_{conf} that appears due to the fact that the internal multiblock chain is stretched and forms a global bridge, the free energy $F_{A,thick}$ of the A-tails and those internal blocks (A-loops) that are inside the thick A-layer, and the free energies $F_{B,thin}$ and $F_{A,thin}$ of the short internal blocks inside the thin central B- and A-layers, respectively,

$$F_{bridge} = (k+1)F_{AB} + F_{conf} + 2F_{A,thick} + \frac{k+1}{2}F_{B,thin} + \frac{k-1}{2}F_{A,thin}. \quad (3)$$

The interfacial free energy F_{AB} can be expressed in terms of the interfacial tension γ and the average area Σ per multiblock copolymer and is given by

$$F_{AB} = \frac{a}{\upsilon}\sqrt{\frac{\chi_{AB}}{6}}\Sigma, \quad (4)$$

where we used $\gamma=(a/\upsilon)\sqrt{\chi_{AB}/6}$. In order to find the conformational contribution F_{conf} we assume that the internal multiblock chain forms only one local bridge per internal domain and the local loops are distributed homogeneously along the multiblock trajectory. Using this simplification the multiblock part can be represented as a chain of k blobs consisting of one bridge and loops and stretched in one direction. The probability of such conformation is $(1/2)^k$, which corresponds to a free energy in k_BT energetic units,

$$F_{conf} = k \ln 2. \quad (5)$$

Next we turn our attention to the free energy of thin and thick domains.

A. Free energy of a thin internal domain

Because the A and B blocks are characterized by the same molecular parameters, the elastic stretching energies of these blocks are equal, i.e., $F_{A,thin}=F_{B,thin}$. Schematically the structure of an internal A-domain is shown in Fig. 3. For the calculation of the elastic free energy of the A-layer, we use the method that has been reported in Refs. 21–23. An A-layer consists of one bridge and loops (Fig. 3). A loop is treated as two linear chains. We introduce α as the fraction of the bridge that is inside the loop region. To satisfy the incompressibility condition we suppose that in the remaining $2H$ region the bridging chains are stretched uniformly, whereas they are nonuniformly stretched in the region where both loops and bridges are present.

The elastic free energy of multiblock chain in one A-layer is given by

$$F_{A,thin} = \frac{6H^2}{a^2 n(1-\alpha)} + \frac{3}{a^2}\int_0^R E_1(z)dz + \frac{6q}{a^2}\int_0^R d\xi\, f(\xi)\int_0^\xi E_2(z,\xi)dz. \quad (6)$$

The first term in Eq. (6) describes uniform stretching of the bridging chain and the second and the third term describe the nonuniform stretching of bridge and loops belonging to one multiblock chain, respectively. $E_1(z)$ is the local tension of that part of the bridge that is nonuniformly stretched, z is the coordinate, $E_2(z)$ is the local tension of the loop whose end (the point of turn) is located at $\xi \leqslant R$, and $f(\xi)$ is the corresponding end-distribution function. Let q denote the average number of loops from each side of the AB interface,

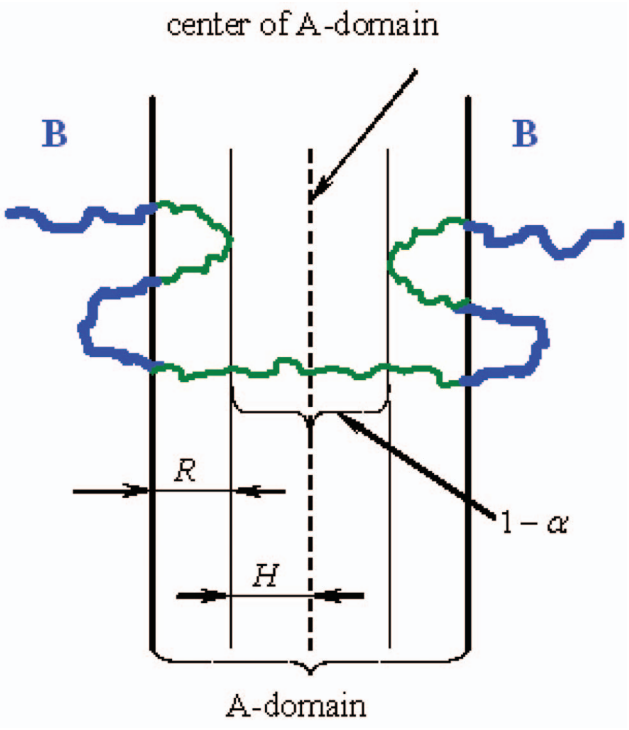

FIG. 3. (Color) Schematic representation of a multiblock copolymer conformation in the A-layer. R denotes the thickness of the loop region, $2H$ is the thickness of the middle part of the A-layer where only bridging chain segments are present, and $1-\alpha$ is the fraction of the bridging segments that are in the $2H$ region.

$$q = \frac{1}{2}\frac{2m+1-k}{k+1}. \quad (7)$$

There are the following constraints for the bridging and looping chains in the A-domain. First, the conservation law of monomers for bridges and loops must be fulfilled, which corresponds to Eqs. (8) and (9), respectively,

$$\int_0^R \frac{dz}{E_1(z)} = \frac{\alpha n}{2}, \quad (8)$$

$$\int_0^\xi \frac{dz}{E_2(z)} = \frac{n}{2}. \quad (9)$$

Next, we have the incompressibility condition that guarantees constant melt density inside the domain,

$$\frac{1}{E_1(z)} + 2q\int_z^R \frac{f(\xi)d\xi}{E_2(z,\xi)} = \frac{\Sigma}{\upsilon}. \tag{10}$$

Minimization of the free energy (6) under the constraints (8)–(10) defines the equilibrium state of the A-domain and yields the local stretching functions as

$$E_1(z) = \frac{\pi}{n}\sqrt{\frac{R^2}{\sin^2(\pi\alpha/2)} - z^2}, \tag{11}$$

$$E_2(z) = \frac{\pi}{n}\sqrt{\xi^2 - z^2}. \tag{12}$$

Substitution of Eqs. (11) and (12) into Eq. (6) leads to the final expression for the free energy of the A-domain,

$$F_{\mathrm{A,thin}} = F_{\mathrm{B,thin}} = \frac{n\upsilon^2 f_1(\alpha)}{a^2\Sigma^2}, \tag{13}$$

with $f_1(\alpha) = (1/\pi)\tan^3(\pi\alpha/2) + (3/\pi)\tan(\pi\alpha/2) + 3(1-\alpha)/2$.

The total thickness of the A-layer is

$$2(R+H) = 2\left(\frac{n\upsilon}{\pi\Sigma}\tan\frac{\pi\alpha}{2} + \frac{n\upsilon(1-\alpha)}{2\Sigma}\right). \tag{14}$$

Using Eq. (14), the probability that a short block is a bridge in the middle B- and A-domains equals

$$p = \frac{H}{(1-\alpha)(R+H)} = \frac{\pi}{\pi(1-\alpha) + 2\tan\dfrac{\pi\alpha}{2}}. \tag{15}$$

Taking into account that the multiblock forms only one bridge per domain, we obtain the equation to find α,

$$\frac{2m+2}{k+1} = 1 - \alpha + \frac{2}{\pi}\tan\left(\frac{\pi\alpha}{2}\right). \tag{16}$$

B. Free energy of thick outer domains

Now we focus our attention on the thick A-domain. Schematically the structure of half of this domain is presented in Fig. 4. It can be considered as an incompressible polymer brush consisting of two types of chains, namely, long A-tails and short A-loops. Similar systems have been considered in Refs. 24–26 where the authors calculated the stretching part of the brush free energy. Generally this energy can be presented as a sum $F_{\mathrm{A,thick}} = F_A + F_\nabla$ of a long-range (stretching) part F_A and a short-range part F_∇ due to the concentration gradient of A-segments belonging to the loops (tails). The sum of these two concentration profiles equals 1.

To calculate the free energy F_A we apply the method that has been presented in Refs. 25 and 26,

$$F_A = F_{\mathrm{tail}} + qF_{\mathrm{loop}}. \tag{17}$$

The free energies F_{loop} of the loop and F_{tail} of the A-tail are given by

$$F_{\mathrm{loop}} = \frac{3}{2a^2}\int_0^{H_2} d\xi\ \eta_1(\xi)\int_0^{\xi} G_1(z,\xi)dz, \tag{18}$$

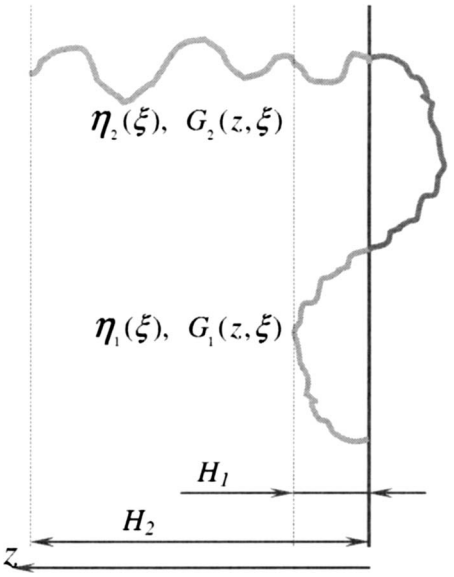

FIG. 4. Schematic representation of the outer part of an A-*b*-(B-*b*-A)$_m$-*b*-B-*b*-A multiblock copolymer conformation. H_1 denotes the thickness of the loop region, H_2 denotes the height of long A-tail. $\eta_1(\xi)$ and $\eta_2(\xi)$ are the loop and A-tail end distribution functions, respectively. Note that $\eta_1(\xi)$ is nonzero only in the H_1 region, whereas $\eta_2(\xi)$ in the same region has zero value. $G_1(z,\xi)$ and $G_2(z,\xi)$ are the functions of local stretching of loop and tail, respectively.

$$F_{\mathrm{tail}} = \frac{3}{2a^2}\int_{H_1}^{H_2} d\xi\ \eta_2(\xi)\int_0^{\xi} G_2(z,\xi)dz. \tag{19}$$

In order to satisfy the incompressibility condition in the outer region, the A-tail is stretched differently in the H_1 and $(H_2 - H_1)$ regions,

$$G_2(z,\xi) = \begin{cases} G_{21}(z,\xi), & z < H_1, \\ G_{22}(z,\xi), & H_1 < z < H_2. \end{cases} \tag{20}$$

The incompressibility conditions thus become

$$\int_{H_1}^{H_2}\frac{\eta_2(\xi)d\xi}{G_{21}(z,\xi)} + 2q\int_z^{H_1}\frac{\eta_1(\xi)d\xi}{G_1(z,\xi)} = \frac{\Sigma}{\upsilon}, \tag{21}$$

$$\int_z^{H_2}\frac{\eta_2(\xi)d\xi}{G_{22}(z,\xi)} = \frac{\Sigma}{\upsilon}. \tag{22}$$

Besides, there are two more constraints to keep the number of monomer units constant,

$$\int_0^{\xi}\frac{dz}{G_1(z,\xi)} = \frac{n}{2}, \tag{23}$$

$$\int_0^{H_1}\frac{dz}{G_{21}(z,\xi)} + \int_{H_1}^{\xi}\frac{dz}{G_{22}(z,\xi)} = N. \tag{24}$$

To find the function of the local stretching, the free energy (17) has to be minimized with respect to $G_1(z,\xi)$ and $G_2(z,\xi)$ under the constraints (21)–(24). Implementation of this procedure by the Lagrange multiplier method immediately yields the next form for the local stretching functions for the A-loops and A-tail, respectively,

$$G_1(z,\xi) = \frac{\pi}{n}\sqrt{\xi^2 - z^2}, \tag{25}$$

$$G_2(z,\xi) = \begin{cases} G_{21}(z,\xi) = \dfrac{\pi}{n}\sqrt{u^2(\xi) - z^2}, & z < H_1, \\ G_{22}(z,\xi) = \dfrac{\pi}{n}\sqrt{u^2(\xi) - u^2(z)}, & H_1 < z < H_2, \end{cases} \tag{26}$$

with

$$u(x) = \frac{x - \lambda\sqrt{x^2 - (1-\lambda^2)H_1^2}}{1-\lambda^2}, \quad \lambda = \frac{2N}{n} - 1. \tag{27}$$

Substitution of Eqs. (25) and (26) into Eq. (17) leads to the expression for the free energy of the outer A-domain in terms of $y = H_1/H_2$,

$$F_A = \frac{\pi^2 \Sigma H_2^3}{2a^2 n^2 (1-\lambda^2)^2}[1 + \lambda^2 - 3\lambda\sqrt{1 - y^2 + \lambda^2 y^2} + \lambda(1 - y^2 + \lambda^2 y^2)^{3/2}]. \tag{28}$$

In order to find y we use the incompressibility condition given by Eq. (21), which yields

$$\sqrt{1 - y^2 + \lambda^2 y^2} - 1 = \frac{(\lambda - 1)qn}{qn + N}. \tag{29}$$

Now let us turn our attention to the analysis of the last gradient term F_∇. The concentration profile of the segments belonging to loops in the region H_1 of the outer A-layer is given by[25]

$$\Phi(z) = \frac{1}{2} + \frac{1}{\pi}\arcsin\frac{2H_1^2 - u^2(H_2) - z^2}{u^2(H_2) - z^2}. \tag{30}$$

This profile results in an additional contribution F_∇ to the total free energy,[27]

$$F_\nabla = \frac{a^2\Sigma}{24\upsilon}\int_0^{H_1} \frac{[\nabla\Phi(z)]^2}{\Phi(z)(1 - \Phi(z))}. \tag{31}$$

This energy diverges at $z = H_1$ because the profile given by Eq. (30) at $z = H_1$ behaves as

$$\Phi(z) = \frac{2\sqrt{2H_1(H_1 - z)}}{\pi\sqrt{u^2(H_2) - H_1^2}}. \tag{32}$$

To avoid this singularity we need to know the real concentration profile $\tilde{\Phi}(z)$ of loops' segments in the vicinity of $z = H_1$. This profile can be expressed in terms of the order parameter $\psi(z)$ satisfying the Schrödinger-type equation,[28]

$$\frac{a^2}{6}\frac{d^2\psi(z)}{dz^2} + (E - \mu(z))\psi(z) = 0, \tag{33}$$

as $\tilde{\Phi}(z) = \psi^2(z)$. Here $\mu(z)$ is the molecular field acting on the segments of loops. It can be obtained from Eq. (25) and in the vicinity of $z = H_1$ has the form

$$\mu(z) = \frac{3\pi^2 H_1}{a^2 n^2}(H_1 - z). \tag{34}$$

Parameter E denotes the "energy" of a loop. After using Eq. (34), the solution of Eq. (33) can be written in terms of the Airy function $\mathrm{Ai}(x)$,[29]

$$\tilde{\Phi}(z) = C\mathrm{Ai}^2[B(z - h_0(E))], \tag{35}$$

where $B = (18\pi^2 H_1/a^4 n^2)^{1/3}$. $h_0 = h_0(E)$ determines the position of profile (35) along the z axis. After joining both profiles Eqs. (32) and (35) (the procedure is described in detail in Appendix A) we arrive at the free energy F_∇,

$$F_\nabla = 0.076\frac{a^2\Sigma}{\upsilon}\sqrt{\frac{BH_1}{u^2(H_2) - H_1^2}}. \tag{36}$$

C. Total free energy per multiblock copolymer chain

Taking into account Eqs. (4), (5), (13), (28), and (36) we can write down the final expression for the free energy per multiblock copolymer chain,

$$F = (k+1)\sqrt{\frac{\chi_{AB}}{6}}\left(\frac{a\Sigma}{\upsilon}\right) + g_1(k,y)\left(\frac{a\Sigma}{\upsilon}\right)^{4/3} + g_2(k,\alpha,y)\left(\frac{a\Sigma}{\upsilon}\right)^2 + (k-1)\ln 2, \tag{37}$$

where

$$g_1(k,y) = 0.36\frac{y^{2/3}(\lambda^2 - 1)}{1 - \lambda\sqrt{1 - y^2 + \lambda^2 y^2}} \times\left(Nn + \frac{n^2}{2}\frac{2m + 1 - k}{k+1}\right)^{-1/3}$$

and

$$g_2(k,\alpha,y) = \frac{\pi^2 N^3}{n^2(\lambda^2 - 1)^2}\left(1 + \frac{n}{2N}\frac{2m + 1 - k}{k+1}\right)^3 \times[1 + \lambda^2 - 3\lambda\sqrt{1 - y^2 + \lambda^2 y^2} + \lambda(1 - y^2 + \lambda^2 y^2)^{3/2}] + \frac{3}{2}Nnk\left[1 - \alpha + \frac{2}{\pi}\mathrm{tg}\frac{\pi\alpha}{2} + \frac{2}{3\pi}\mathrm{tg}^3\frac{\pi\alpha}{2}\right].$$

The free energy (37) is a function of the variables α, y, Σ, k and parameters λ, m, χ_{AB}. To determine α and y Eqs. (16) and (29) are used. The minimization of the total free energy with respect to the interface area Σ per copolymer chain gives its equilibrium value. As a result we obtain the free energy of the A-b-(B-b-A)$_m$-b-B-b-A copolymer chain as a function of the number k of internal layers for given values of m, λ, and χ_{AB}. For different numbers of m the equilibrium number of k is determined by the minimal value of the corresponding free energy.

The results of the numerical calculations are presented and discussed in the next section.

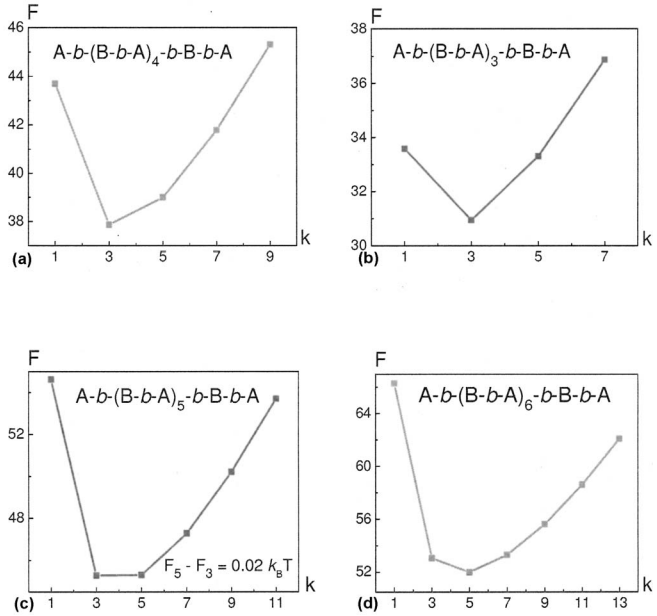

FIG. 5. Free energy F of the A-b-(B-b-A)$_m$-b-B-b-A multiblock copolymer as a function of the number k of internal layers for $\chi_{AB}n=24.3$, $n/N=0.26$. (a) $m=4$, (b) $m=3$, (c) $m=5$, and (d) $m=6$.

III. RESULTS AND DISCUSSIONS

Numerical calculations have been performed first for the experimental situation corresponding to the PS-b-[(PI-b-PS)$_4$-b-PI]-b-PS multiblock copolymers. From the experimental data we have that $\chi_{AB}n=24.3$, $n/N=0.26$, $\chi_{AB}=0.1$.[5] In this case the free energy behaves as shown in Fig. 5(a). We see that the minimal value of the free energy corresponds to a number of internal domains $k=3$, in excellent agreement with experiment.[5] Similar calculations have been done for different values of $m=3$, 5, and 6. The corresponding equilibrium numbers of internal layers are $k=3$, 3, and 5. The respective plots of the free energy as a function of k are presented in Figs. 5(b)–5(d). The values of k at the minima of $F(k)$ for the binary system and for similar ternary systems with P2VP end blocks[23] are given in Table I. Note that for the binary multiblock copolymer with $m=5$ the free energies of the three-layered and five-layered structure are very close to each other, as indicated in Fig. 5(c).

We see that compared to the ternary system, the number of internal layers in the binary system is obviously reduced due to the possibility of having loops in the outer domains. This causes a concentration gradient in these domains with a corresponding loss of conformation entropy. This contribution turns out to be quite essential. Neglecting this gradient term gives $k=1$ as the optimal number of internal domains for all values of m, in conflict with the available experimental data. Taking the gradient contribution into account (quantitatively this contribution scales as $\Sigma^{4/3}$, where Σ is interfacial area), we effectively create an additional interface area that is essential for the layer formation.

TABLE I. Number of internal layers k for binary and ternary systems. [The values for the ternary systems are taken from our previous paper (Ref. 23).]

A-b-(B-b-A)$_m$-b-B-b-A		C-b-(B-b-A)$_m$-b-B-b-C	
m	k	m	k
3	3	3	5
4	3	4	5
5	3	5	7
6	5	6	7

TABLE II. Number of internal layers for A-b-(B-b-A)$_m$-b-B-b-A multiblock copolymer for $\chi_{AB}=0.1$ and different values of n/N.

n/N	$m=3$	$m=4$	$m=5$	$m=6$
0.05	1	3	3	3
0.1	3	3	3	3
0.2	3	3	3	5
0.26	3	**3**	3	5
0.5	3	3	5	5

A. Analysis for selected systems

To investigate the effects of elastic stretching and interfacial tension we subsequently performed calculations for different values of n/N and different values of χ_{AB}. We start with considering different values of n/N with the length of internal blocks fixed and Flory–Huggins interaction parameter $\chi_{AB}=0.1$. The number of lamellar domains for $m=3,4,5,6$ and $n/N=0.05;0.1;0.2;0.26;0.5$ are given in Table II. The corresponding free energies for $m=3$ and $m=6$ are represented in Figures 6(a) and 6(b). The squared symbols depict the minimum of the free energies and thus the optimal number of lamellar domains, under the assumption that this lamellar morphology remains indeed the equilibrium morphology. Bold case in Table II reflects the experimental case described in Ref. 5.

Similar calculations have been performed for $\chi_{AB}=0.4$ with $m=3,4,5,6$ and $n/N=0.05;0.1;0.2;0.26;0.5$ and fixed length of the internal blocks. The minima of the corresponding free energies appear at the values of k presented in Table III. The free energies for $m=3$ and $m=6$ are represented in Figs. 7(a) and 7(b).

Comparison of Table II and III shows that for $\chi_{AB}=0.1$ there are more possibilities to get a five-layered structure, whereas for $\chi_{AB}=0.4$ there are more possibilities to get only one internal domain. In both cases the three-layered structure is dominant. From a comparison of Tables II and III for a fixed ratio of n/N we observe the tendency for a decreasing optimal number of domains for increasing Flory–Huggins parameter values, i.e., then AB-interactions become more unfavorable. This is related to the fact already discussed in the Introduction, that short A-chains from the middle part of the multiblock start to go to the outer A-domain when χ_{AB} increases. Note that the behavior of ternary C-b-(B-b-A)$_m$-b-B-b-C multiblock copolymers will be exactly the opposite: since none of the middle A- and B-blocks can be in the outer C-part, increasing χ_{BC} will create more internal domains.

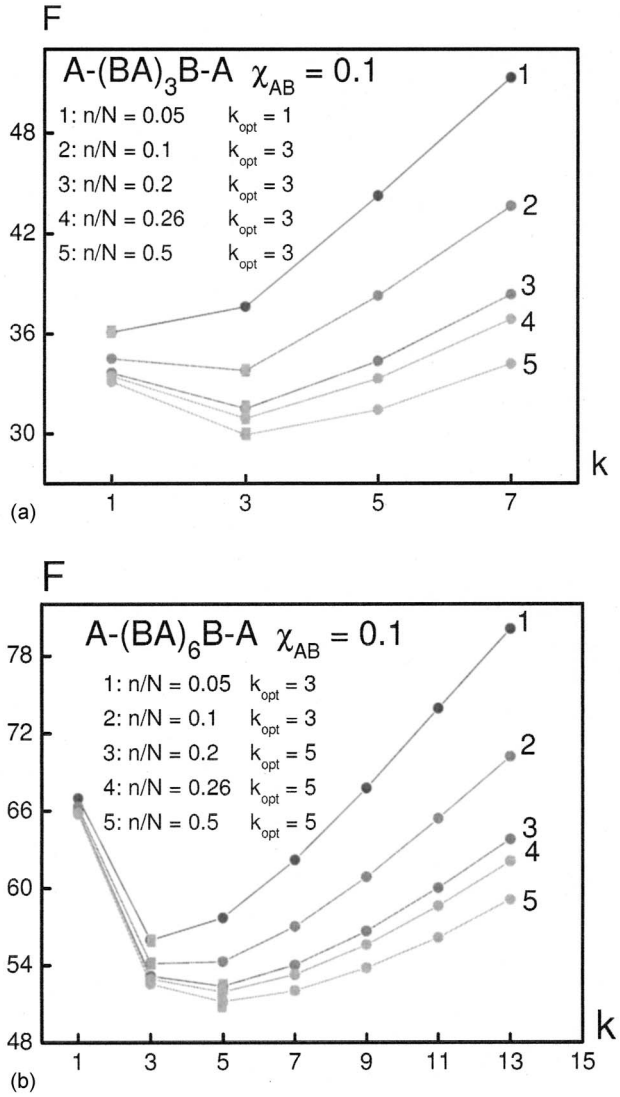

FIG. 6. Free energy F of the A-b-(B-b-A)$_m$-b-B-b-A multiblock copolymer as a function of the number k of internal layers for $\chi_{AB}n=24.3$ and different values of n/N. (a) $m=3$; (b) $m=6$.

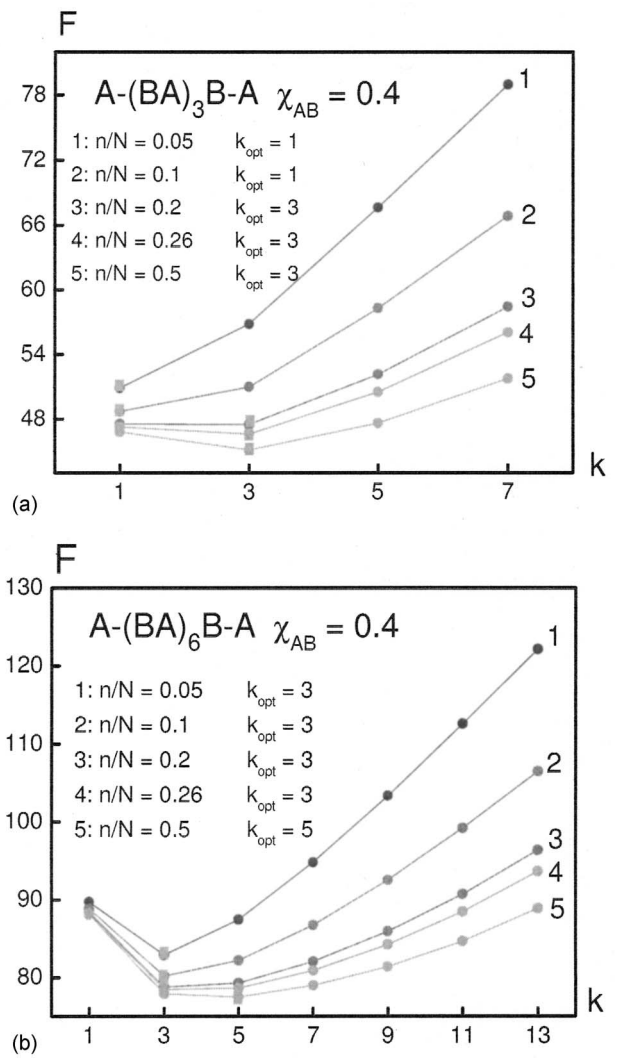

FIG. 7. Free energy F of the A-b-(B-b-A)$_m$-b-B-b-A multiblock copolymer as a function of the number k of internal layers for $\chi_{AB}n=97.2$ and different values of n/N. (a) $m=3$; (b) $m=6$.

IV. CONCLUDING REMARKS

In this paper, we presented a theoretical analysis of binary A-b-(B-b-A)$_m$-b-B-b-A multiblock copolymer melts. Considering the lamellar-in-lamellar self-assembled state we addressed the question of the number k of internal layers as a function of the number m of repeating middle (B-b-A) units. Applied to a specific case, we showed that the result of our numerical calculations was in excellent agreement with the available experimental data.

TABLE III. Number of internal layers for A-b-(B-b-A)$_m$-b-B-b-A multiblock copolymer for $\chi_{AB}=0.4$ and different values of n/N.

n/N	$m=3$	$m=4$	$m=5$	$m=6$
0.05	1	1	3	3
0.1	1	3	3	3
0.2	3	3	3	3
0.26	3	3	3	3
0.5	3	3	3	5

We demonstrated that to a large extent the domain formation is determined by the interplay between interfacial forces and elastic stretching of the individual blocks. The combinatorial contribution corresponding to the number of different possibilities to create global loops or bridges was taken into account in an approximate manner.

Compared to a ternary system where all middle blocks are located in between the outer long end blocks, the binary system is considerably more complicated. The important new element in the analysis of the binary system concerns the conformational contribution associated with the concentration gradient of A segments in the outer A-domain belonging to long tail A-blocks and short middle A-blocks. This gives an additional interfacial area depending contribution that is essential for the internal domain formation. Without this term the minimum of the free energy invariably occurs at $k=1$ internal thin layers.

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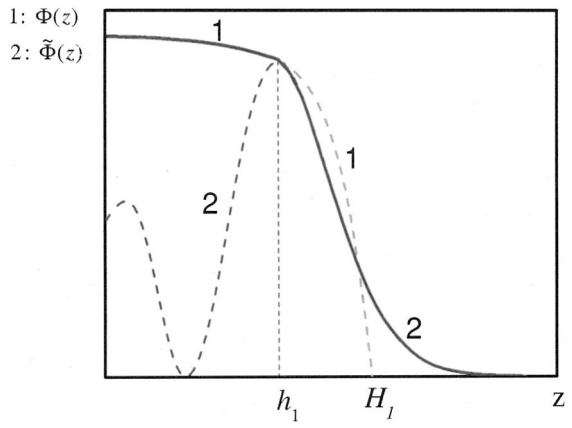

FIG. 8. Schematic presentation of $\Phi(z)$ (line 1) and $\tilde{\Phi}(z)$ (line 2). The solid line corresponds to the joint profile that is used for the calculation of the conformational free energy.

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APPENDIX: CALCULATIONS OF THE CONFORMATIONAL FREE ENERGY

In the vicinity of $z=H_1$ the profile $\Phi(z)$ of segments belonging to loops in the outer A-region obtained using the strong stretching limit has the form (32),

$$\Phi(z)=\frac{2\sqrt{2H_1(H_1-z)}}{\pi\sqrt{u^2(H_2)-H_1^2}}.$$

On the other hand the form of this profile $\tilde{\Phi}(z)$ follows from the solution of the Schrödinger-type equation (33) in the molecular field $\mu(z)$ given by Eq. (35),

$$\tilde{\Phi}(z)=C\mathrm{Ai}^2[B(z-h_0(E))].$$

Schematically the behavior of the functions $\Phi(z)$ and $\tilde{\Phi}(z)$ is presented in Fig. 8.

At $z=h_1$ profile 1 transforms into profile 2,

$$\Phi(h_1)=\tilde{\Phi}(h_1). \tag{A1}$$

Moreover, in order to have a smooth profile, the derivatives of $\Phi(z)$ and $\tilde{\Phi}(z)$ at $z=h_1$ have to be equal also

$$\Phi'(h_1)=\tilde{\Phi}'(h_1). \tag{A2}$$

The conservation of monomer units implies

$$\int_{h_1}^{H_1}\Phi(z)dz=\int_{h_1}^{\infty}\tilde{\Phi}(z)dz. \tag{A3}$$

Equations (A1)–(A3) allow us to find h_0, h_1, and C. Substitution of Eqs. (32) and (35) into Eqs. (A1)–(A3) and further simplifications lead to

$$\int_{-t_B}^{\infty}\mathrm{Ai}^2(x)dx+\frac{1}{6}\frac{\mathrm{Ai}^3(-t_B)}{\mathrm{Ai}'(-t_B)}=0, \tag{A4}$$

where $t_B=B(h_0-h_1)$. The numerical solution of Eq. (A4) yields

$$h_0-h_1=0.806/B. \tag{A5}$$

Further using Eqs. (A1) and (A2) one gets

$$H_1-h_1=1.267/B, \tag{A6}$$

$$C=\frac{3.6886H_1}{\sqrt{BH_1[u^2(H_2)-H_1^2]}}. \tag{A7}$$

The conformational free energy is given by

$$F=F_\nabla^1+F_\nabla^1=\frac{a^2\Sigma}{24\upsilon}\int_0^{h_1}\frac{[\nabla\Phi(z)]^2}{\Phi(z)(1-\Phi(z))}dz+\frac{a^2\Sigma}{24\upsilon}\int_{h_1}^{\infty}\frac{[\nabla\tilde{\Phi}(z)]^2}{\tilde{\Phi}(z)(1-\tilde{\Phi}(z))}dz. \tag{A8}$$

Taking into account Eqs. (A5) and (A7) we obtain

$$F_\nabla^1=\frac{a^2\Sigma}{24\upsilon}\int_0^{h_1}\frac{[\nabla\Phi(z)]^2}{\Phi(z)(1-\Phi(z))}dz\approx 0.017\frac{a^2\Sigma}{\upsilon}\sqrt{\frac{BH_1}{u^2(H_2)-H_1^2}}. \tag{A9}$$

Once $h_0-h_1=0.806/B$ is known, the general form of profile (35) can be specified as

$$\tilde{\Phi}(y)=C\mathrm{Ai}^2(By-0.806), \tag{A10}$$

where $y=z-h_1$ and the constant C is determined according to Eq. (A7). Using this, the second part of the conformational free energy equals

$$F_\nabla^2=\frac{a^2\Sigma}{24\upsilon}\int_0^{\infty}\frac{[\nabla\tilde{\Phi}(y)]^2}{\tilde{\Phi}(y)(1-\tilde{\Phi}(y))}dy\approx 0.059\frac{a^2\Sigma}{\upsilon}\sqrt{\frac{BH_1}{u^2(H_2)-H_1^2}}. \tag{A11}$$

The total conformational energy is thus given by

$$F_\nabla=F_\nabla^1+F_\nabla^2=0.076\frac{a^2\Sigma}{\upsilon}\sqrt{\frac{BH_1}{u^2(H_2)-H_1^2}}. \tag{A12}$$

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